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Determination of the activation energy of surface states by electric – field – induced current (EFIC) technique

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Abstract : Trap activation energies are generally measured by thermally stimulated current (T.S.C.) techniques. But for cases where trap-activation energy itself depends on temperature, the T.S.C. method fails. In this experiment, induced current is measured during filling up of emptied traps by changing electric field using a pen-recorder polarograph and activation energy is measured by a simple method which does not depend on the model of the barrier profile.

Keywords : Zinc oxide, surface states, activation energy.

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1. Introduction

Surface states present in large numbers on semiconducting metal-oxide surfaces can lock barrier height to a fixed value irrespective of the work-functions of the contacting metals. Using point contact probes, both barrier heights for the metal-semiconducting metal oxide contact and activation energy for slow surface traps on oxdies can be measured by trapping and detrapping of electrons (Dimaria and Stasiak 1989). For slow surface states such mechanisms (i.e. rate of trapping as well as detrapping) are found to depend exponentially on the applied voltage. Thus the traps can be emptied by applying reverse voltage for a sufficiently long period of time while the current can be measured by filling the traps during forward biasing condition (when the metal tip is negative). If the voltage is increased at a sufficiently high rate from zero voltage (after fully detrapping the charges in the surface states) then the i-v characteristics (forward) gives a measure of the activation energy for the slow surface states. Thus Electric Field Induced Current (EFIC) during trapping and detrapping mechanism can be used to measure the activation energy of the slow surface states. This new method would be most effective

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where the trap activation energy is a function of temperature and also in cases where structure of the oxide (anodic) changes with temperature. In this paper, the activation energy of the slow surface states on an anodic zinc oxide has been determined keeping the sample at room temperature (27°C). The value of the activation energy obtained from i-v characteristics during this filling up of traps (empty) is compared with the threshold energy required by electrons for the start of current creep phenomena.

2. Experimental

ZnO is deposited on mother zinc by using pure zinc (99.9% purity) as an anode in an alkaline electrolytic bath with platinum plate as cathode. Zinc oxide being amphoteric in nature, it grows to a certain thickness, after which there is no more deposition. At this point, the rate of oxide formation is balanced by the rate of dissolution of the oxide in the electrolyte. The metal tablet (about 1 cm^2 facial area) is then quickly taken out and washed in flowing de-ionized water. It is then taken out, dried in air and mounted in an ebonite structure and a metal point probe is gently pressed on to it. The current voltage and current creep characteristics are traced using a pen recorder polarograph (Cambridge C 603282). During the experiment, the contact mounted firmly in an ebonite structure, is kept in a closed dark chamber.

3. Experimental results and discussions

Figure 1 describes the i-v characteristics at different stages of preparation (curves

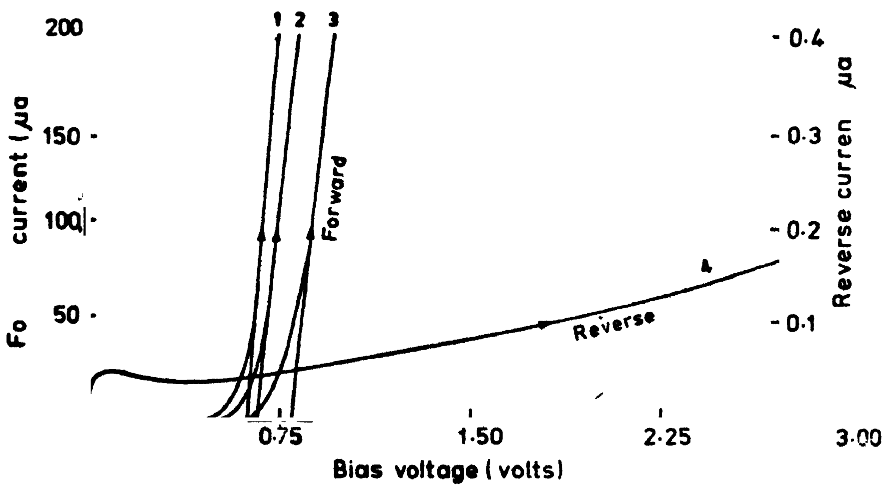

Figure 1. Forward (Curves 1, 2, 3) and reverse (Curve 4) i-v characteristics. For as-prepared ZnO-metal contact (Curve 1) and after 1 minutes voltage formation of the junction (Curve 2). Curves (3) and (4) are after semiformation of the junction.

1 and 2) and semiformed (curve 3) point contact. Curve (1) is for the virgin sample (as prepared ZnO). Next the junction is kept at +3 volt bias for about 1 minute and the i-v characteristic (2) is obtained. Next the point contact is kept at +3 volt bias for about 15 minutes and then the i-v (3) is obtained. It is found that the same i-v curve is repeated if the junction is kept under forward +3 volt bias for 20 minutes, 25 minutes or even longer times. It is seen that during 20 minutes of +3 volt bias, forward current falls from 10 ma to 5 ma. Thus the (i-v) curve (3) describes the i-v characteristics of semi-permanent formation stage of the point contact. During tracing of the i-v curves the voltage ramp is at the rate of 0.005 volt per second.

The barrier height for as fabricated contact is about 0.63 eV (curve 1) and that for junction after 1 minute of voltage formation (Henisch 1957) is about 0.66 eV (curve 2) and for the semiformed contact is about 0.78 eV (curve 3). The reverse characteristics (4) for the semiformed junction is shown in the same graph. The small hump near the origin (for reverse i-v) shows the condenser-type action of the contact followed by more or less a linear rise indicating constant resistance behaviour of reversedly biased junction as described by Mott (Henisch 1957). Rectification ratio at 0.79 volt is of the order of 500.

Figure 2 represents the i-v characteristics for the semiformed junction after however, sealing the as-fabricated junction with wax to protect it from changing

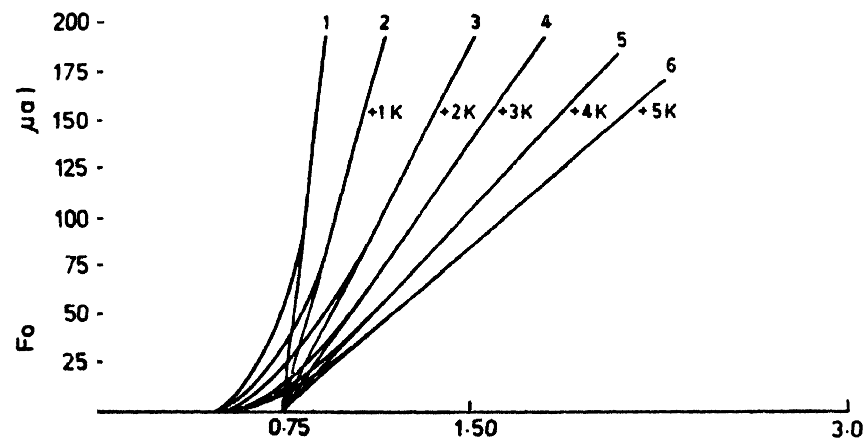

Figure 2. Forward i-v characteristics with different external resistances put in series with the point contact (labelled in the diagram). Curve (1) is without any external series resistance.

local environment and it is kept in dark chamber at 300 K for about 24 hours. Then the junction is again semiformed by keeping it under 3 volts forward bias for sufficient times. During tracing of all the curves by the penrecorder, voltage is increased from 0 value at the rate of 0.005 volt per second through the built-in-devices within tha cambridge pen recorder polarograph (Model C 603282). The curves 1, 2, 3, 4, 5, 6 are drawn taking resistances 0, 1kΩ, 2kΩ, 3kΩ, 4kΩ, 5kΩ, respectively in series with the point contact. The curves are extrapolated to meet the voltage axis at about 0.75 volt. This method is a slight modification of that developed by Cooper (1952) and is independent of any model of the barrier profile.

Figure 3 also represents the forward i-v characteristics with voltage ramp of 0.005 volt per second. Here, at first the junction is kept under 3 volt reverse bias

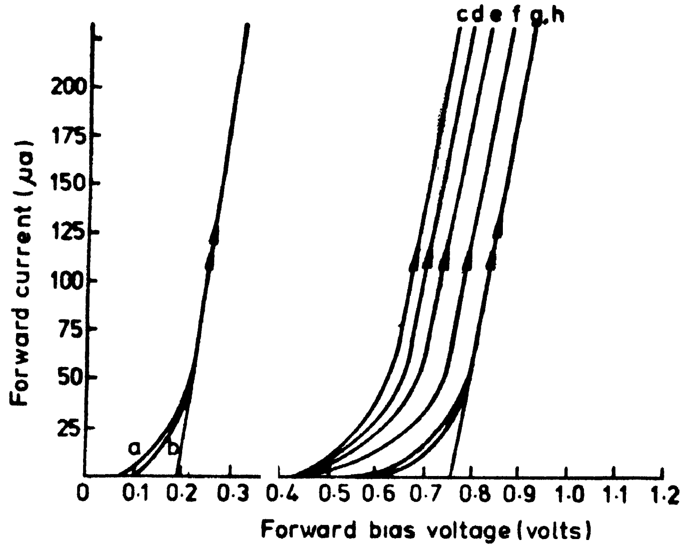

Figure 3. Curves a, b represent the i-v characteristics during removal of trapped electrons from negatively charged surface states, c, d, e, f represent the intermediate characteristics including bulk conduction and surface states contribution to the current while curves (g), (h) represent the final steady characteristics.

for about 1 minute and curve (b) is obtained and then the junction is put to same reverse bias for about 10 minutes and the curve (a) is obtained. The same curve (a) is repeated if the junction is kept at reverse 3 volts bias for longer times. Now the junction is kept under forward bias of 3 volts for about 1, 2, 3, 4, 5, 6, 10, 15, 30 minutes respectively. And in each case forward i-v curves (a, b, c, d, e, f, g, h) are obtained just immediately after the reverse voltage stresses on the junction are withdrawn. Curves g, h, falls on one another at least as far the straight portions of the curves are concerned. The curves g, h, are of same nature as curve (1) of Figure 2 and again gives same barrier height as already obtained (Figure 2). Curves (a), (b) of Figure 3 are of much importance. When the junction is kept under reverse bias voltage (sufficiently small not to cause any catastrophic breakdown) the metal point contact is positive. The negative oxide surface ejects hot electrons from the O^- traps (These O^- states are most likely formed on the surface when the oxide was used as an anode in the electrolyte due to liberation of electronegative oxygens in the vicinity of the oxide). Thus the traps are emptied when the junction is put under reverse bias. So when the junction is immediately put under forward bias, these emptied traps would be filled up. As the surface traps have generally got small activation energy they are rapidly filled up by hot electrons. If the voltage is increased from zero as the electrons flow, would follow the same exponential rule to fillup the traps as followed while surmounting over any potential barrier. The straight portions of a, b, when extrapolated, meet the voltage axis at about 0.19 volt. It gives a measure of activation energy (0.19 eV) of the slow surface states formed on anodic zinc oxides. The voltage being automatically increased at the rate of 0.005 volt per second the pen recorder takes time only about 40 seconds to trace the complete curves (a) or (b).

In Figure 4 the forward current creep curves are drawn. Here the junction is put under different forward biases of 0.05, 0.1, 0.2, 0.25, 0.30, 0.35 volt

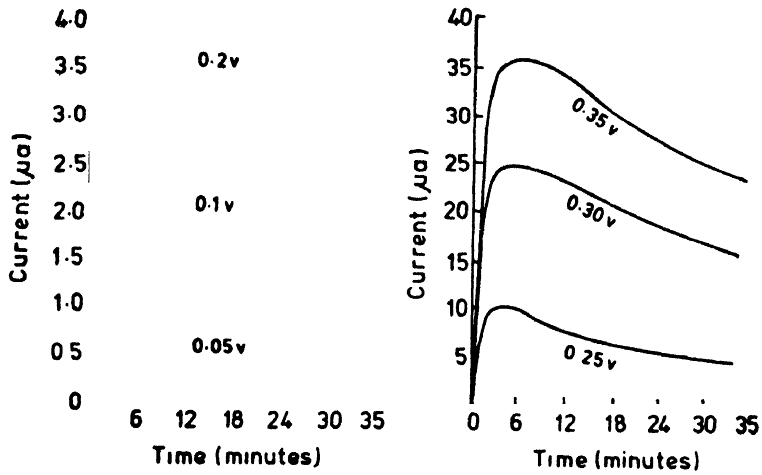

Figure 4. Current creep curves at different forward bias voltages.

respectively. And the change of current is noted as a function of time. There is no current creeps at 0.05 and 0.1 volt, it starts from voltage at about 0.2 volt and there are appreciable current creeps at 0.25, 0.30, 0.35 volts and larger forward bias voltages. In each case, the junction is kept under short-circuit condition for about 5 minutes before the tracing of each $(i\text{-}t)_v$ curves. Under forwardly biased condition, the metal point contact is negative. Hence at a particular voltage, the neutral surface traps (O centres) capture electrons and that is why initial current is greater. The process is somewhat like charging of a condenser in parallel with a variable resistance. However, below 0.2 volt there is practically no current creep. This (0.2 volt) may be called the threshold voltage for the current creep process in zinc oxide-metal contact. It is to be noted that current creeps are appreciable above 0.2 volt viz. at 0.25, 0.30, 0.35 volts respectively. This shows that electrons with energy $\gtrsim$ 0.2 eV can surmount over the potential barrier of the surface states and take part in creeping processes. This is in accordance with the value of the activation energy which is about 0.19 eV for the oxyginated surface states on anodic zinc oxide as obtained from Figure 3. On the other hand in T.S.C. technique the carriers trapped at low temperatures are freed from the traps during the heating cycle (Pickard and Davis 1979) and the peaks in the current vs temperature curves indicate the presence of discrete trapping levels.

5. Conclusions

The top surface of the anodic zinc oxide is of *p*-type nature due to excess oxygen in interstitial positions and/or Zn^{+} ion vacancies. The value of the surface barrier height for the semiformed contact is about 0.78 eV which accords to the value (0.75 eV) obtained by the authors (Sengupta and Chatterjee 1982) in their earlier report. The activation energy of slow surface traps obtained from the transient i-v characteristics for the fully de-trapped junction is 0.19 eV. And this tallies well with the minimum voltage (0.2 volt) required for the starting of the current creep phenomena in this particular junction.

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